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(54) **Process for producing coated papers and coated cardboards endowed with barrier properties against the migration of water vapour, and so obtained products.**

(57) Process for producing coated papers and coated cardboards endowed with properties of barrier against the migration of water vapour, which consists in generating on the surface of paper and/or cardboard, at least one layer based on vinyl polymers and/or copolymers, in submitting the surface of the so-treated paper and/or cardboard to a suitable surface treatment for modifying its structure and for rendering said surface wettable by water-based dispersions, preferably consisting in submitting said surface to a corona-effect electrical discharge, and in generating at least one further layer by means of the spreading of conventional coating substances, with a layer of "pre-coat" being possibly interposed between bare cardboard and said polymer-based layer.

Coated papers and cardboards with barrier properties obtained by means of said process.

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PROCESS FOR PRODUCING COATED PAPERS AND COATED CARDBOARDS ENDOWED WITH BARRIER PROPERTIES AGAINST THE MIGRATION OF WATER VAPOUR, AND SO OBTAINED PRODUCTS

The present invention relates to a process for producing coated papers, coated light cardboards and coated cardboards endowed with barrier properties against the migration of water vapour.

The coated papers and cardboards endowed with marked barrier properties obtained by means of such a process are another object of the present invention.

Said coated cardboards, and similar products, are used, with considerable advantages of usefulness and cheapness, in packing industry and in general in the protective packing of materials or substances which require a protection, during their transport, storage, and so forth, against the entry of moisture inside the interior of the packaged product units, as such a need arises, for exemplifying purposes, in case of cleansing agents and the like, alimentary products, hygroscopic organic and inorganic substances for industrial use, for use in agriculture, and so forth.

Within the present invention, the term "cardboard and similar products" is used in order to mean all of the types of paper, light cardboard and cardboard, which are normally used for packing the various types of products.

It is well-known that cardboards destined to the production of packages is submitted, after its manufacture as a raw material, to subsequent processing steps aiming at giving the same cardboard different quality characteristics and/or levels, according to the envisaged end use, such as calendering, embossing, coating, rolling, printing, decorative printing, and so forth.

In particular the coating operation substantially consists in an operation by means of which the surface of the raw cardboard is coated, e.g., by means of rolls or of air blades or inert-gas blades, with coating products used as aqueous emulsions or suspensions, which are thus spread on cardboard in order to yield various layers or thicknesses, obtained by means of a same number of "passes", according to the forecast cardboard use. The coating is usually adopted in order to fill the interstices between fibres, so as to equalise and smooth the cardboard surface, endowing it with the desired decorative characteristics, with characteristics of sight and touch pleasantness and, above all, in order to allow cardboard to be printed, e.g., according to rotogravure or offset printing processes.

The coating products are normally constituted by kaolin, carbonates, sulfates (barium sulfate, alkali-earth metal sulfates, and so forth), TiO_2 , and so forth, in a finely subdivided form, either alone,

or associated with one another to form mixtures, and kept dispersed in an aqueous solution by means of suitable dispersant substances, such as water-soluble polymers of methacrylic acid, such as polymethacrylates, sodium hexametaphosphate, and so on, and associated with other components, according to the use the end product is intended for.

For orientative purposes, said dispersions contain from 50 to 70% of solid coating material, with the balance being constituted by water, the dispersant agent, and the other additives, such as whiteners, binding agents, and so forth.

When cardboard is expected to oppose water vapour passage, in that it is destined to the production of, e.g., packages for hygroscopic or anyway moisture-sensitive substances, with the risk of a qualitative decay of the contained product from the chemical and/or physical viewpoint (blocking, loss of free-flowing characteristics, and the like), as it typically is the case of the cleansing agents and of similar products, the manufacturers have to resort to special impermeabilizing processes.

In order to endow cardboard with characteristics of resistance to the passage of water vapour according to the techniques known from the prior art, the cardboard sheet is "coupled" with preformed sheets or films of metal materials or of plastic materials, such as aluminum, polyethylene, copolymers of vinylidene chloride and the like, with "composite" or "sandwich" cardboards being thus obtained, which are constituted by at least one cardboard layer or one or more layers of preformed sheets of such impermeable materials. In general, said composites enable the problem of preventing water vapour from passing through cardboard to be satisfactorily solved, but require particular processing procedures, to be carried out with delicate, and often laborious techniques.

In order to give cardboard a certain resistance to the passage of water vapour, in some cases the same print protective lacquers can be used, i.e., those transparent lacquers, of various types, e.g., on an acrylic base, which are applied on coated and printed cardboard sheet at the end of the same printing step. In this way, a certain barrier effect against the passage of moisture is obtained which is anyway by far lower than as reached by using the coupling technique as hereinabove reminded. The process is moreover very burdensome, in that a plurality of lacquer layers have to be applied; besides all, the application of a plurality of layers of protective lacquer at the end of the printing step obliges the manufacturer to renounce to an equiv-

alent number of applications of coloured inks, and therefore also causes limitations of aesthetical character.

Furthermore, when cardboard is submitted to plying, creasing, and similar operations in order to produce shaped packages, e.g., of box shape, microfractures occur often in the protective/barrier layer at the corners and at the creases, which microfractures irreparably compromise the effectiveness of the whole barrier layer; in fact, those skilled in the art know well that it is enough that water vapour comes into contact with the underlying cardboard in just one point, for water to uniformly diffuse over time throughout the cardboard sheet, dampening it.

A process which is the subject-matter of a prior patent application filed with the Italian Patent Office under application No. 20375 A/88 on April 29th, 1988, in the same Applicant's name, which makes it possible a coated cardboard to be obtained with good barrier properties against water vapour migration and with good characteristics of mechanical strength and of printability, consists in depositing on bare cardboard a first layer of a mixture constituted by a dispersion of pigments or fillers and by a suspension/emulsion of a binding/impermeabilizing agent based on vinyl-acrylic copolymers or the like, in superimposing to this first layer a second layer of pigment-free binding/impermeabilizing agent, and in finally applying one or more coating layer(s) of a known type.

A purpose of the instant invention is of providing a process for producing coated cardboard endowed with barrier properties against the migration of water vapour, which is not affected by the drawbacks hereinabove reminded for the prior art.

Another purpose is of providing a coated cardboard endowed with barrier properties which additionally to the barrier properties against moisture and water vapour passage shows very good surface characteristics, which can be printed by means of commonly used technologies and using printing apparatuses and products, such as inks, lacquers, and so forth, as normally used for coated cardboards and, finally which can be packages, containers and the like, by using the known technologies and without that its original characteristics of impermeability are even only partially compromised. These, and still other purposes which can be better evidenced by the following disclosure, are achieved by means of a process for producing a coated cardboard endowed with barrier properties against the migration of water vapour, which process, according to the present invention, comprises the following steps:

A) on the surface of the sheet of paper or of cardboard, at least one layer is spread, which is

constituted by an aqueous dispersion of polymers and/or copolymers and/or of other polymeric and/or polymerizable compounds;

B) after drying, the surface of the sheet of cardboard treated according to said (A) step is submitted to a suitable treatment for modifying the reticulated surface structure and lowering the surface tension thereof, so as to render said surface easily wetted by water-based solutions and/or dispersions;

C) on the surface of the sheet of cardboard treated according to said (A) and (B) steps, at least one layer is finally spread of an aqueous dispersion of one or more pigment(s) of the type normally used for the conventional coating of paper, and comprising dispersants and binding agents of a known type.

Said pigments of the type as normally used for paper coating are constituted, e.g., by kaolin, calcium carbonate, titanium dioxide and the like, in a finely subdivided form, anyway such as to be capable of being dispersed in aqueous suspension and of being maintained in such a dispersed form by means of suitable dispersing agents, such as, e.g., the water-soluble polymers of methacrylic acid, sodium hexametaphosphate, and the like.

Said aqueous suspension of polymers and/or copolymers and/or other polymeric and/or polymerisable compounds can be advantageously constituted by an aqueous dispersion of vinyl polymers and copolymers, selected from among the group consisting of vinylidene chloride, polymers of the type used for antiblocking coatings for paper, cloths and the like, vinyl chloride, vinyl acetate, and the like.

A composition used for accomplishing said (A) step, according to the present invention, is constituted by an aqueous dispersion comprising copolymers of vinylidene chloride with methyl acrylate and acrylonitrile, containing about 50% of dry matter, such as, e.g., the dispersion available on the market under the mark "DIOFAN" 193 D (Registered trade mark by BASF Aktiengesellschaft).

More particularly, said treatment suitable for modifying said surface structure, and for rendering the surface of the sheet of cardboard treated according to said (A) step wettable by water-based solutions and/or dispersions consists in submitting said surface to the action of an electrical discharge with corona effect, with the same sheet being laid on an electrical conducting metal armature kept, according to known processes, at a high potential, so that the electrostatic pressure at its surface exceeds the dielectric strength of air, thus generating the well-known ionizing effluve.

Other treatments also suitable for modifying the reticulated structure of the surface of the sheet

and for rendering it wettable by the water-based solutions and/or dispersions base are those which consist in submitting the same surface to the fast action of a flame or of an arc discharge (I.R. radiation), or to the action of ionizing radiations, and the like. The process according to the present invention is preferably carried out as a continuous process, by arranging in series the various equipment pieces used for spreading the aqueous dispersions and for drying them, as well as the equipment piece, of known type, for carrying out the suitable treatment for modifying the surface structure of the sheet according to above (B) step.

The process according to the present invention makes it possible paper or cardboard to be obtained, which is endowed with very good barrier properties against the migration of water vapour, while simultaneously showing very good characteristics of printability, both from a qualitative viewpoint and from the viewpoint of the rendering of colours, and so forth. The present Applicant was able to observe indeed that the corona-effect discharge according to the (B) step of the present invention causes a change to occur in the surface tension of the surface of cardboard treated with said dispersion of vinyl polymers according to said (A) step, with said cardboard surface becoming perfectly compatible with the aqueous coating dispersion which is spread on it, according to the above step (C), so that an evenly distributed coating is obtained, which does not show any irregularities or unevennesses and is therefore suitable for receiving, even after long time periods and with extremely good results, any types of printed patterns of decorative printed patterns, of lacquers, of colours, and the like, according to usual technologies of known type, using normal apparatuses, also known and commonly used, and furthermore using printing products such as inks, lacquers, dyes and the like, of the normally and commonly used type for printing normal coated cardboard.

In order to further improve the wettability of cardboard surface treated according to said (A) and (B) steps, besides the dispersants and the binding agents of known type, also non-foaming surfactants, preferably alcohol-based non-foaming surfactants, such as based, e.g., on butyl alcohol, isopropyl alcohol, and so forth, can be added to the aqueous dispersion of pigment according to said (C) step.

Still according to the present invention, on the surface of the sheet of "bare" or "raw" cardboard, a first coating layer can be spread, which consists of an aqueous dispersion of one or more pigments of the type normally used for paper coating in paper industry, and comprising dispersants and binding agents of known type, which constitutes a base layer onto which the layer constituted by the

dispersion of polymers and/or copolymers according to said (A) step is spread, after said first coating layer being preliminarily dried.

The presence of pigments in said "pre-coating" layer, which is spread on bare cardboard before said (A) step, performs, above all, the task of causing the between-fibre microchannels existing on cardboard surface to be occluded, thus preventing said layer which is applied at a later time, according to step (A), and constituted by impermeabilizing polymers and copolymers, from being absorbed inside the underlying cardboard mass and of consequently making it possible a continuous film to be obtained from said polymer layer, which continuous film maximizes the properties of impermeability to water vapour.

In fact, it is known that water vapour crosses cardboard both flowing through between-fibre pores and through the same fibres. The only way by means of which cardboard can be given properties of resistance to passage of water vapour is therefore that of coating the surface of the same cardboard with a continuous film of a substance impermeable to water vapour, which completely covers the surface of said cardboard, as well as any fibres protruding outwards from the same surface.

In that way, impermeabilized cardboards for packaging purposes are obtained with degree of impermeabilization of the same order of magnitude as obtainable by operating according to the prior art in the composite cardboards produced by means of the above disclosed "sandwich" technique with a polyethylene layer.

The raw cardboard which constitutes the substrate of the coated cardboard is constituted by any materials as used in the prior art for producing coated cardboards, independently from the more or less substantial or exclusive presence of cellulosic natural fibres, of synthetic fibres, and so forth, provided they are compatible with a conventional coating operation.

The present invention furthermore relates to coated paper and/or cardboard endowed with barrier properties against the migration of water vapour obtained according to the hereinabove disclosed process, which coated papers and/or cardboards comprise, according to the present invention:

- at least one first layer constituted by an impermeabilizing material constituted by different polymers and/or copolymers,
- at least one further layer of a conventional coating, comprising pigments and other additives known from the prior art.

According to a different form of practical embodiment of the present invention, and still within the scope thereof, the coated papers and cardboards endowed with barrier properties against the

migration of water vapour obtained according to the hereinabove disclosed process, comprise:

- a first layer directly applied on the surface of the sheet of raw paper or cardboard, with said layer being constituted by a coating of the type normally used for paper coating;
- at least one second layer constituted by an impermeabilizing material constituted by different polymers and/or copolymers,
- at least one further layer of a conventional coating, comprising pigments and other additives known from the prior art.

Said polymers, copolymers and polymer blends are preferably selected from the group comprising the vinyl polymers, and, in particular, vinylidene chloride polymers and copolymers with methyl acrylates and/or acrylonitrile, and the like.

The present Applicant was also able to observe that cardboard obtained according to the instant invention can be submitted to the necessary mechanical operations for producing boxes, packages and the like and, in particular, to creasing operations, without its characteristics of impermeability and of barrier against passage of water vapour are endangered.

The impermeabilizing agents applied to cardboard as above said are compatible with the mixtures of materials which constitute the conventional coating layers, which therefore have not to comply with special requisites.

Degrees of impermeability comprised within the range of from 10 to 20 are reached, wherein said degrees of impermeability are expressed as "barrier to water vapour", as measured according to the standard procedure TAPPI T 646, OS-73 Official Standard - 1973 (and TAPPI T 533 pm-76). The tests were carried out with a moisture gradient of 90% and at the temperature of 38°C. This degree of impermeability can only be reached, according to the present state of available technology, with composite materials consisting of a sandwich structure of cardboard/polyethylene/paper. Of course, to the instant finding as hereinabove disclosed structurally and functionally equivalent modifications and variants may be supplied, without departing from the scope of protection of the same finding.

Claims

1. Process for manufacturing coated papers and coated cardboards endowed with properties of barrier against the migration of water vapour, characterized in that it comprises the following steps:

A) on the surface of the sheet of paper or of cardboard, at least one layer is spread, which is constituted by an aqueous dispersion of polymers

and/or copolymers and/or of other polymeric and/or polymerizable compounds;

B) after drying, the surface of the sheet of cardboard treated according to said (A) step is submitted to a suitable treatment for modifying the reticulated surface structure and lowering the surface tension thereof, so as to render said surface easily wettable by water-based solutions and/or dispersions;

C) on the surface of the sheet of cardboard treated according to said (A) and (B) steps, at least one layer is finally spread of an aqueous dispersion of one or more pigment(s) of the type normally used for the conventional coating of paper, and comprising dispersants and binder agents of a known type.

2. Process for manufacturing coated papers and coated cardboards endowed with barrier properties according to claim 1, characterized in that said dispersion of polymers and copolymers according to said (A) step is constituted by an aqueous dispersion of vinyl polymers and/or copolymers, selected from the group comprising vinylidene chloride, vinylidene chloride with methyl acrylate and acrylonitrile, vinyl chloride and vinyl acetate.

3. Process according to claim 1, characterized in that said treatment suitable for modifying said surface structure, and for rendering the surface of the sheet of paper and/or cardboard treated according to said (A) step wettable by water-based solutions and/or dispersions consists in submitting said surface to the action of an electrical discharge with corona effect, with the same sheet being laid on a electrical conducting metal armature kept, according to known processes, at a high potential.

4. Process according to claim 1, characterized in that said treatment suitable for modifying said surface structure and for rendering the surface of the sheet of paper and/or cardboard treated according to the (A) step wettable by the water-based solutions and/or dispersions is selected from the group which comprises the treatment consisting in submitting said surface to the fast action of a flame or of an arc discharge (I.R. radiation), and the treatment consisting in submitting said surface to the action of ionizing radiations.

5. Process according to claim 1, characterized in that said aqueous dispersion of one or more pigment(s) according to the (C) step also comprises, besides dispersants and pigments of known type, non-foaming surfactant products.

6. Process according to claim 5, characterized in that said non-foaming surfactant products are alcohol-based surfactants, i.e., based on such an alcohol as butyl alcohol, isopropyl alcohol, and the like.

7. Process according to claim 1, characterized

in that on the surface of the sheet of "bare" or "raw" cardboard, a first layer of "pre-coating" is spread, which consists of an aqueous dispersion of one or more pigments of the type normally used for paper coating in paper industry, and comprising dispersants and binding agents of known type, which constitutes a base layer onto which the layer constituted by the dispersion of polymers and/or copolymers according to said (A) step is spread, after said first pre-coating layer being preliminarily dried.

8. Process according to claim 1, characterized in that said layers of several polymers and copolymers and of coating are applied by spreading by means of rolls and/or air blades according to traditional processes known in the art.

9. Process according to claim 1, characterized in that it is carried out according to a continuous process.

10. Coated paper and/or cardboard endowed with barrier properties against the migration of water vapour, characterized in that it comprises:
- at least one first layer constituted by different polymers and/or copolymers,
- at least one further layer of a conventional coating, comprising pigments and other additives known from the prior art.

11. Coated paper and/or cardboard endowed with barrier properties against the migration of water vapour, characterized in that it contains:
- a first layer of a conventional coating, or "pre-coating", directly applied on the surface of the raw sheet;
- at least one second layer constituted by different polymers and/or copolymers,
- at least one further layer of a conventional coating, comprising pigments and other additives known from the prior art.

12. Coated paper and/or cardboard according to claims 10 and 11 characterized in that said different polymers and/or copolymers are selected from the group comprising the vinyl polymers and, in particular, polymers and copolymers of vinylidene chloride with methyl acrylates and/or acrylonitrile.

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